

Thermal Properties of Blends of Poly(hydroxybutyrate-*co*-hydroxyvalerate) and Poly(styrene-*co*-acrylonitrile)

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ABSTRACT: Thermal properties of blends of poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) and poly(styrene-*co*-acrylonitrile) (SAN) prepared by solution casting were investigated by differential scanning calorimetry. In the study of PHBV-SAN blends by differential scanning calorimetry, glass transition temperature and melting point of PHBV in the PHBV-SAN blends were almost unchanged compared with those of the pure PHBV. This result indicates that the blends of PHBV and SAN are immiscible. However, crystallization temperature of the PHBV in the blends decreased approximately 9–15°. From the results of the Avrami analysis of PHBV in the PHBV-SAN blends, crystallization rate constant of PHBV in the PHBV-SAN blends decreased compared with that of the pure PHBV. From the above results, it is suggested that the nucleation of PHBV in the blends is suppressed by the addition of SAN. From the measured crystallization half time and degree of supercooling, interfacial free energy for the formation of heterogeneous nuclei of PHBV in the PHBV-SAN blends was calculated and found to be 2360 (mN/m)³ for the pure PHBV and 2920–3120 (mN/m)³ for the blends. The values of interfacial free energy indicate that heterogeneity of PHBV in the PHBV-SAN blends is deactivated by the SAN. This result is consistent with the results of crystallization temperature and crystallization rate constant of PHBV in the PHBV-SAN blends. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 673–679, 2000

Key words: poly(hydroxybutyrate-*co*-hydroxyvalerate); poly(styrene-*co*-acrylonitrile); blend; biodegradable polymer; thermal property

INTRODUCTION

Poly(hydroxybutyrate) (PHB), an aliphatic polyester synthesized by bacterial fermentation, is known to degrade fully in the environment without forming any toxic products.¹ This biodegradable nature of the PHB is very important from the point of view of reducing plastic wastes. Recently, for the purpose of commercial use, scientific and technical researches about the PHB have been widely investigated.^{1–14} However, there are sev-

eral shortcomings to the commercial use of the PHB. Because it is produced from microorganisms, it is relatively expensive compared with other biodegradable polymers. Also it is rather brittle for use below the glass transition temperature (T_g) and can be easily degraded thermally above melting point. To reduce its brittle character, various copolymers that have different types of aliphatic polyester units, for example poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) have been biosynthesized.^{1,5–8}

Another approach to modifying the properties of PHB and PHBV is to form polymer blends with synthetic or biodegradable polymers. Through blends with other polymers, the cost of the final materials can be reduced and the mechanical

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Table I Characteristics of Polymer Samples Used in the PHBV-SAN Blends

	\overline{M}_w	\overline{M}_n	T_g (°C) ^a	T_m (°C) ^a	T_c (°C) ^a
PHBV ^b	470,000 ^c	127,000 ^c	5.2	151.2	97.0
SAN ^d	116,600 ^e	41,800 ^e	99.7	—	—

^a Measured in our laboratory by DSC.

^b Supplied by Imperial Chemical Industries, London.

^c Data from Ref. 5.

^d Supplied by Miwon Petrochemicals Co., Korea.

^e Measured in our laboratory by GPC.

properties of the PHB and PHBV can be improved. Many investigators have studied thermal behavior, crystallization, and mechanical properties of blends of the PHB with synthetic and other biodegradable polymers such as poly(ethylene oxide),^{9,10} poly(vinyl acetate),¹¹ poly(vinyl alcohol),¹² cellulose ester,¹³ and poly(ϵ -caprolactone) (PCL).¹⁴ In this article, we investigate the effect of poly(styrene-*co*-acrylonitrile) (SAN) on the crystallization behavior of PHBV in the PHBV-SAN blends. Thermal and crystallization behavior of PHBV-SAN blends prepared by solution casting was studied using differential scanning calorimetry (DSC). Also, the crystallization kinetics of the PHBV-SAN blends was analyzed by using the Avrami equation¹⁵ and the nucleation theory.¹⁶

EXPERIMENTAL

Polymers

The polymers used in this study were obtained from commercial sources. The characteristics and sources of the polymer samples used in this study are shown in Table I. The PHBV were manufactured by Imperial Chemical Industries under the trade name of Biopol (7 mol % HV content). SAN (28% AN content) was supplied by Miwon Petrochemical Co.

Blend Preparations

Blends of the two polymers were prepared by solution casting. For solution casting, a total of 0.6 g of the PHBV/SAN mixture was dissolved in 20 mL of chloroform at room temperature [3.0% (w/v) solution] for at least 1 day. Blends were cast on glass plates, and all film samples were dried under vacuum for 7 days at room temperature.

Thermal Analysis

The thermal properties of all samples were analyzed by using a Perkin-Elmer differential scanning calorimeter, Model DSC-7. Temperature calibration was performed using indium [melting temperature (T_m) = 156.6°C, ΔH_f = 28.5 J/g]. To measure the melting temperature and crystallization temperature of the PHBV-SAN blends, blend samples of 5 to 15 mg were heated in a nitrogen atmosphere from -40°C to 175°C at a heating rate of 20 K/min and then cooled to -40°C at a rate of 20 K/min. T_g of PHBV in the blends was obtained from the heating scan at a heating rate of 20 K/min after rapidly cooling to -40°C.

Isothermal crystallization experiments of the PHBV in the blends were performed on DSC. For the isothermal crystallization of the blends, samples were melted at 175°C for 3 min, and then rapidly cooled to the isothermal crystallization temperature. From the isothermal crystallization experiments, the crystallization kinetic data such as crystallization half time, crystallization rate constant, and Avrami exponent were obtained.

A thermogravimetric analyzer (TGA) was used to investigate the thermal stability of the PHBV-SAN blends. The weight loss with temperature was assessed with a DuPont TGA. Measurements were conducted in air at a heating rate of 20 K/min.

RESULTS AND DISCUSSION

Thermal Behavior of PHBV-SAN Blends

Thermal behavior of the PHBV-SAN blends was studied using DSC. The effect of blend composition on the T_g of PHBV in the blends is shown in Figure 1. In Figure 1, it can be seen that the T_g of PHBV in the blends is almost unchanged com-

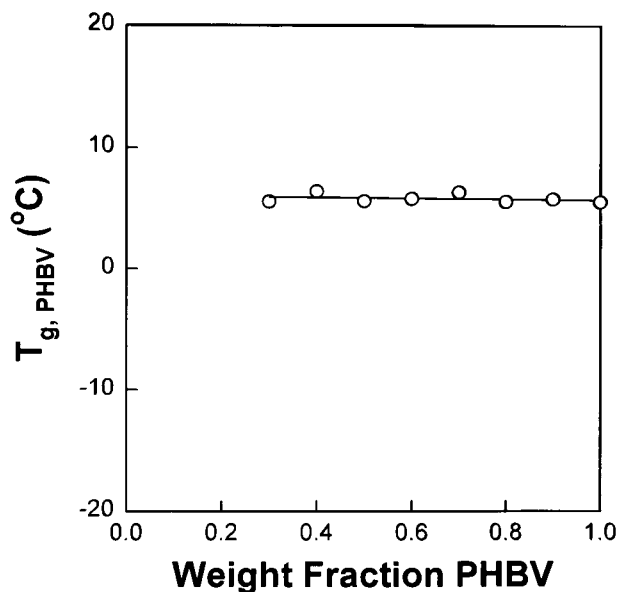


Figure 1 Effect of blend composition on the T_g of PHBV in the PHBV-SAN blends.

pared with the pure PHBV. Figure 2 shows the DSC heating thermograms of 1.0, 0.9, 0.7, 0.5, 0.3, and 0.0 weight fraction PHBV in the PHBV-SAN blends. In Figure 2, it can be seen that the T_m of the PHBV in the blends is almost unchanged compared with that of the pure PHBV. The results of

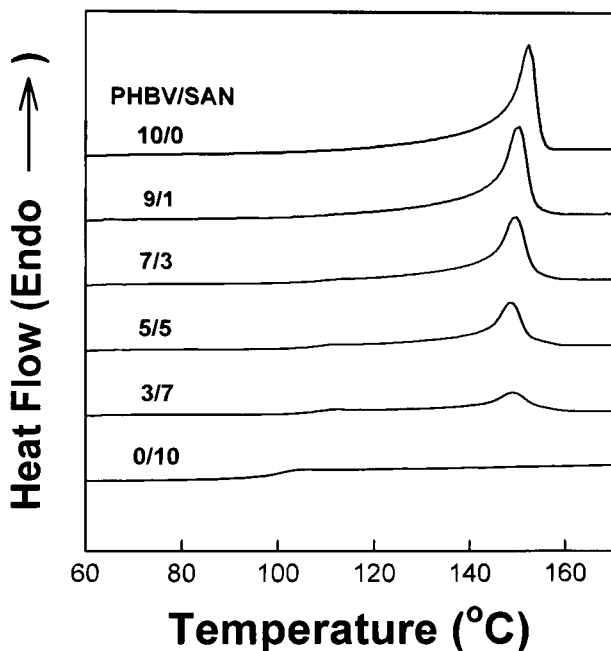


Figure 2 DSC heating thermograms of the PHBV-SAN blends.

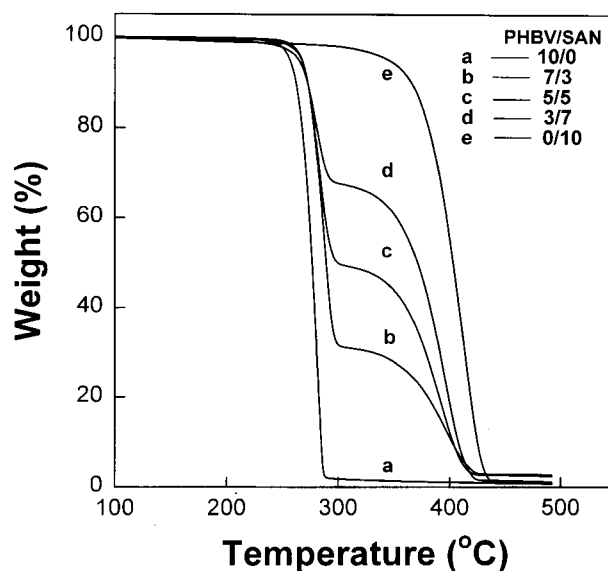


Figure 3 TGA curves for the PHBV-SAN blends.

T_g (PHBV) and T_m (PHBV) in the blends indicate that the blends of PHBV and SAN are immiscible under the mixing condition.

TGA was used to investigate the thermal stability of the PHBV-SAN blends. The TGA results of 10:0, 7:3, 5:5, 3:7, and 0:10 PHBV-SAN blends are shown in Figure 3. It is shown that the onset degradation temperature of the pure SAN has a higher value than that of the pure PHBV. For the PHBV-SAN blends, a two-step weight loss was observed with the weight fraction of SAN. In Figure 3, the onset degradation temperature of the PHBV-SAN blends was shown to almost unchanged compared with that of the pure PHBV. Cheung and Stein¹⁷ have studied the phase behavior of miscible blends of PCL and polycarbonate (PC). From the TGA result of PCL-PC blends, they have reported that the onset degradation temperature of PCL-PC blends increased almost linearly with increasing PC weight fraction. Therefore, the TGA result of PHBV-SAN blends indirectly suggests that the two polymers are immiscible, which is consistent with the results of T_g (PHBV) and T_m (PHBV) in the PHBV-SAN blends.

The DSC cooling thermograms of 1.0, 0.9, 0.7, 0.5, and 0.3 weight fraction PHBV in the PHBV-SAN blends are shown in Figure 4. For the pure PHBV, the crystallization temperature (T_c) taken as a maximum of the crystallization exotherm was observed at 97°C. In Figure 4, the T_c of PHBV in the blends decreased approximately 9–15° more than the T_c of the pure PHBV. The decrease of the T_c (PHBV) in the PHBV-SAN blends sug-

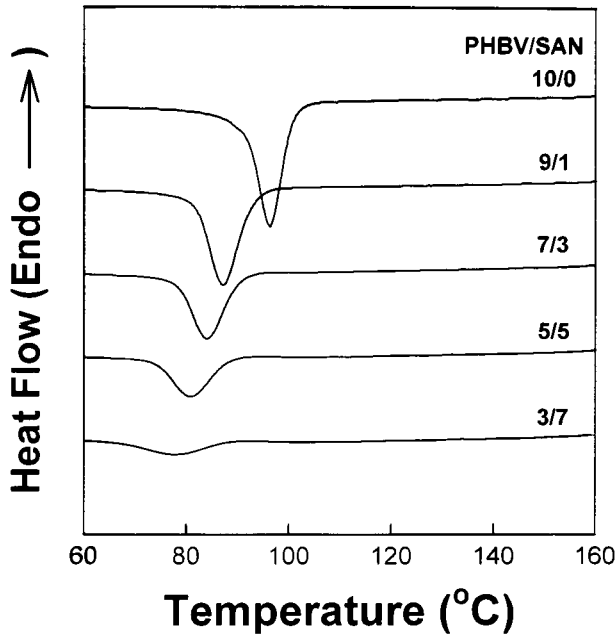


Figure 4 DSC cooling thermograms of the PHBV-SAN blends.

gests that the SAN affects the crystallization behavior of PHBV in the PHBV-SAN blends. The effect of SAN on the crystallization behavior of the PHBV will be discussed in the next section.

Isothermal Crystallization of PHBV-SAN Blends

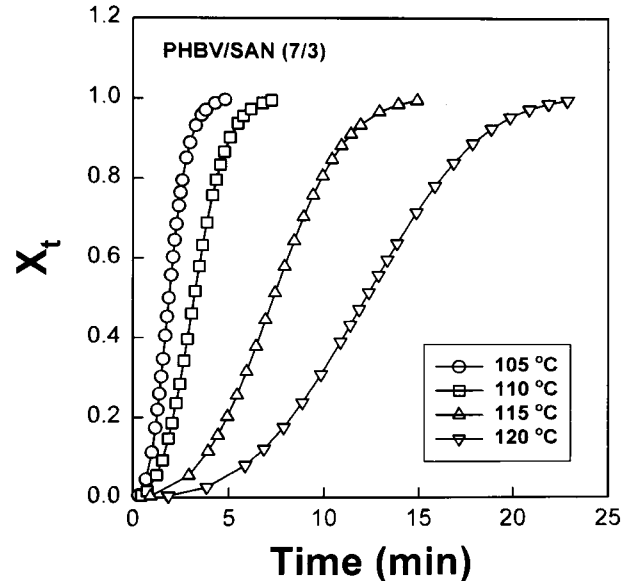
The crystallization kinetics of the PHBV in the PHBV-SAN blends was analyzed by using the Avrami equation¹⁵:

$$\log[-\ln(1 - X_t)] = \log K_n + n \log t \quad (1)$$

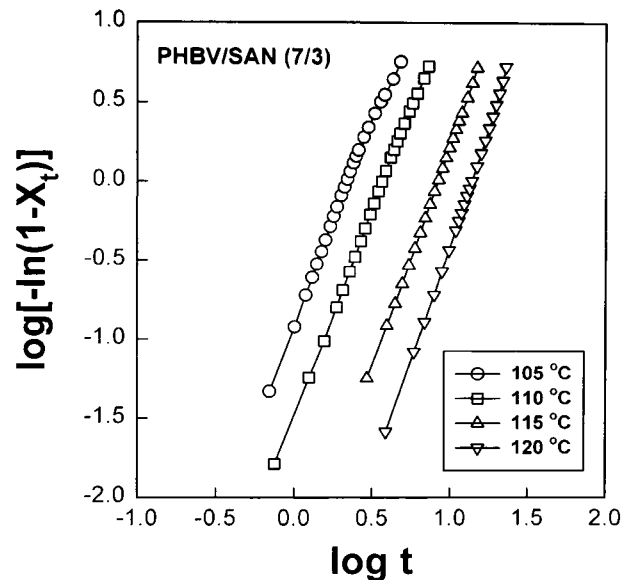
where X_t is the weight fraction of crystallinity at time t , n is the Avrami exponent, and K_n is the overall crystallization rate constant. The weight fraction of crystallinity vs time and Avrami plots of PHBV in the 7:3 PHBV-SAN blends are shown in Figures 5(a) and (b), respectively. From the Avrami plots of PHBV in the PHBV-SAN blends, the n and K_n were obtained and are shown in Table II. For the PHBV-SAN blends, the Avrami exponent of the PHBV was found to range from 2.6 to 3.0 with isothermal crystallization temperature. The Avrami exponent of pure PHBV is approximately 3.0, which indicates three-dimensional spherulitic growth from instantaneous nuclei.

In Table II, it can be seen that the K_n of PHBV in the PHBV-SAN blends has lower value than

that of the pure PHBV. In the Avrami analysis, it is known that the Avrami exponent and crystallization rate constant depend on nucleation, growth rate, and dimensions of the crystals. The decrease in crystallization rate constant for the PHBV-SAN blends indicates that the nucleation of the PHBV in the blends is suppressed by the addition of SAN. Such results can be explained by



(a)



(b)

Figure 5 Isothermal crystallization kinetics data for the 7:3 PHBV-SAN blends: (a), plots of X_t vs time; (b), Avrami analysis.

Table II Crystallization Rate Constant (K_n) and Avrami Index (n) of PHBV in the PHBV-SAN Blends at Different Crystallization Temperatures

T_c (°C) ^a	PHBV		PHBV/SAN (9 : 1)		PHBV/SAN (7 : 3)	
	K_n ^b	n ^c	K_n ^b	n ^c	K_n ^b	n ^c
105	1.02×10^{-5}	3.11	5.63×10^{-6}	2.65	2.02×10^{-6}	2.69
110	3.94×10^{-6}	2.96	1.77×10^{-6}	2.63	4.85×10^{-7}	2.70
115	1.62×10^{-6}	2.80	2.92×10^{-8}	2.89	2.52×10^{-8}	2.81
120	2.20×10^{-7}	2.80	8.71×10^{-9}	2.84	2.41×10^{-9}	2.95

^a Isothermal crystallization temperature.

^b Overall crystallization rate constant (sec⁻ⁿ). Data were calculated from eq. (1).

^c Avrami index. Data were calculated from eq. (1).

the negative effect of the SAN on the primary nucleation of the PHBV.

It is known that the presence of a second component in polymer blends has a great effect on the primary nucleation of the crystallizing component.¹⁸ The influence of the second component in the blend on primary nucleation of the crystallizing component depends on the chemical structure of the polymer, miscibility and its ability to crystallize, blend composition, and conditions of the mixing process. When the polymer blends are miscible, the energy barrier for the formation of a critical nucleus in the blends is greater than that of the homopolymer.¹⁹ Therefore, nucleation activity of heterogeneous nuclei and the number of heterogeneous nuclei active in the blends generally decrease with increasing the concentration of a second polymer in the blends.

For the immiscible blends, the deactivation of heterogeneity was reported by Martuscelli et al.²⁰ and Galeski et al.²¹ For blends of polypropylene (PP) and low density polyethylene (LDPE), they have reported that the number of heterogeneous primary nuclei of PP decreases with increasing concentration of LDPE in the blends. They have explained that this result is due to the migration of heterogeneity from PP toward LDPE. The driving force for such migration of the heterogeneity would be the difference in interfacial free energies of the impurities in both components. Therefore, in this study, whereas the PHBV is immiscible with the SAN, the deactivation of heterogeneity in PHBV in the PHBV-SAN blends can be explained by the migration of the heterogeneity from the PHBV to the SAN.

Nucleation of PHBV in PHBV-SAN Blends

In primary nucleation processes, heterogeneous nucleation takes place if performed nuclei or for-

eign surfaces are present. From the nucleation theory, the probability for the presence of a nucleus of given size is proportional to $\exp(-\Delta G/kT)$.¹⁶ For the heterogeneous nucleation, the number of heterogeneous nuclei able to participate in nucleation (N) can be expressed by eq. (2) in terms of the free energy for formation of the nucleus and activation energy of the diffusion.

$$N \approx \exp[-(\Delta G^* + \Delta G_\eta)/kT] \quad (2)$$

where N is the nuclei per unit volume, k is the Boltzmann constant, ΔG^* is the free energy for formation of a nucleus from the melt, and ΔG_η is the activation energy of the diffusion. When the supercooling decreases or isothermal crystallization temperature decreases, the ΔG_η can be considered as a constant. In general, the heterogeneous nucleation occurs at a low degree of supercooling, therefore in eq. (2), the ΔG_η is almost constant.

In eq. (2), the free energy for formation of a heterogeneous nucleus from the melt at an undercooling is given by eq. (3)¹⁶:

$$\Delta G^* = 16\Delta\gamma\gamma_e(T_m^0)^2/(\Delta H_f\Delta T\rho_c)^2 \quad (3)$$

where T_m^0 is the equilibrium melting temperature, ΔH_f is the heat of fusion, γ and γ_e are the surface free energies parallel and perpendicular to the molecular chain direction between the crystal and its own melt, respectively, and $\Delta\gamma$ is the specific interfacial free energy difference parameter.

In three-dimensions, spherulitic growth can be treated similarly to the rain drops problem, developed by Evans.²² If nucleation is assumed to lead to negligible amounts of crystal formation and athermal (all N nuclei per unit volume are

performed and active at time zero), the volume fraction of the material which crystallized at time t can be written as follows²³:

$$v^c = 1 - \exp(-4\pi NG^3 t^3/3) \quad (4)$$

where v^c is the volume fraction of the material crystallized, G is the linear growth rate of polymer crystal (assumed to constant). For the spherulitic growth from instantaneous nuclei, the v^c can be expressed by the Avrami equation as follows:

$$v^c = 1 - \exp(-K_n t^3) \quad (5)$$

Also, eq. (5) can be expressed in terms of crystallization half time ($t_{0.5}$) as follows:

$$v^c = 1 - \exp(-0.693t^3/t_{0.5}^3) \quad (6)$$

From eqs. (2–6), the relationship between ΔG^* and $t_{0.5}$ are given by eq. (7):

$$\ln t_{0.5} = A + \Delta G^*/3kT \quad (7)$$

where A is the temperature independent constant. From the isothermal crystallization experiments of the PHBV-SAN blends, the $t_{0.5}$, which is defined as the time required to attain a relative crystallinity of 50%, was obtained. From eq. (7), the interfacial free energy for formation of heterogeneous nucleus of PHBV in the PHBV-SAN blends can be calculated. The values of PHBV of $T_m^0 = 450$ K, $\Delta H_f = 132$ J/g, and $\rho_c = 1.25$ g/cm³ were used for calculation.⁵ The plots of $\ln t_{0.5}$ vs $1/T\Delta T^2$ are shown in Figure 6. From the slopes of the plots of $\ln t_{0.5}$ vs $1/T\Delta T^2$, the values of $\Delta\gamma\gamma_e$ were found to be 2360, 2980, 2920, and 3120 (mN/m)³ for the 10 : 0, 9 : 1, 7 : 3, and 5 : 5 PHBV-SAN blends, respectively. Organ and Barham⁵ have studied nucleation, growth, and morphology of poly(hydroxybutyrate) and its copolymers (PHBV). From the growth and nucleation rate measurements by optical microscopy, they have reported that the surface free energy for homogeneous nucleation of PHBV (7 mol % HV content) is 3115 (mN/m)³. It is known that heterogeneous nucleation path makes use of foreign preexisting surfaces to reduce the free energy for nucleation opposing primary nucleation.¹⁶ Therefore, for the heterogeneous nucleation, a lower overall free energy for nucleation is needed than the homogeneous nucleation. From the results of $\Delta\gamma\gamma_e$ of the

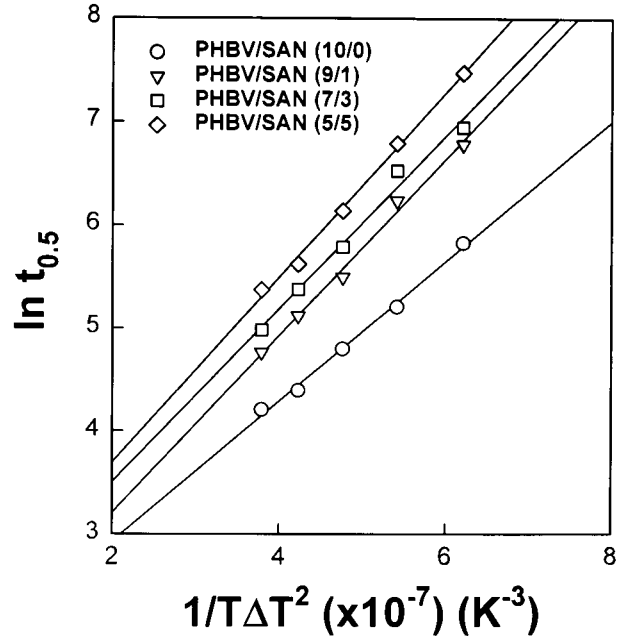


Figure 6 Effect of degree of supercooling on the crystallization half time ($t_{0.5}$) of the PHBV-SAN blends. The lines represent the linear regression results.

pure PHBV, it appears that the interfacial free energy of pure PHBV is lower than the result by Organ and Barham.⁵

The interfacial free energy for the formation of the nucleus is related to the nucleating activity.¹⁶ From the above results, the increase in interfacial free energy of PHBV in the PHBV-SAN blends compared with that of the pure PHBV suggests that the heterogeneity of the PHBV in the PHBV-SAN blends is deactivated by the SAN. Therefore, the formation of heterogeneous nucleus of PHBV in the PHBV-SAN blends would be more difficult than the pure PHBV. This result is consistent with the results of the crystallization temperature and the crystallization rate constant of PHBV in the PHBV-SAN blends. From the above results, it is suggested that crystallization of the PHBV in the PHBV-SAN blends is suppressed by the presence of SAN.

CONCLUSIONS

In the thermal analysis of PHBV-SAN blends by DSC, T_g (PHBV) and T_m (PHBV) in the PHBV-SAN blends are almost unchanged compared with those of the pure PHBV. This result leads to the conclusion that the blends of PHBV and SAN are

immiscible. T_c of PHBV in the PHBV-SAN blends decreased approximately 9–15° more than the T_c of the pure PHBV.

From the isothermal crystallization studies of PHBV in the PHBV-SAN blends, crystallization rate constant of PHBV in the PHBV-SAN blends decreased compared with that of the pure PHBV. From these results, it is concluded that the nucleation of PHBV in the blends is suppressed by the addition of SAN.

From the measured crystallization half time and degree of supercooling of PHBV in the blends, interfacial free energy ($\Delta\gamma\gamma_e$) for the formation of heterogeneous nuclei of PHBV in the PHBV-SAN blends was calculated and found to be 2360 (mN/m)³ for the pure PHBV and 2980–3120 (mN/m)³ for the blends. The values of interfacial free energy indicate that heterogeneity of PHBV in the PHBV-SAN blends is deactivated by the SAN, which is consistent with the results of crystallization temperature and crystallization rate constant of PHBV in the PHBV-SAN blends.

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